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2

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ABSTRACT $1 \, 3/ \, 7 \, 8$

An empirical description of the shape of certain optical absorption bands in ionic crystals is proposed. The new formula links a nearly Gaussian description of the band near its maximum with an exponential description of the band on the low energy tail (Urbach's rule). For the I^--absorption band in KCl and the exciton bands in pure alkali halides the applicability of the proposed shape formula over a wide range of absorption constants is demonstrated. A review of the theoretical background which led to the proposed description is given.

INTRODUCTION

Electronic transitions in ionic crystals give rise to very broad absorption bands of halfwidth 0.1 to 1 eV in the range of photon energy of 1 to 10 eV. Especially in alkali halide crystals a large variety of these bands has been investigated. The two major types are absorption centers arising from vacancies filled with electrons or holes (F- and V-type centers) and absorption centers which consist of added impurity ions, most of them of the same valency and incorporated substitutionally in the host lattice ($T\bar{l}$, I^-, $B\bar{r}$, OH^-, and H^- in KCl for example). For the F-centers in alkali halides[1] and the Tl-ion in KCl[2] the shape and the halfwidth of the absorption or emission bands were studied at various temperatures. It was observed that in these cases a <u>Gaussian</u> <u>curve</u> fits the data rather well. The temperature variation of the halfwidth can be fit by a law: $H^2(T) = H^2(0) \coth (\frac{\hbar\omega}{2kT})$, to the degree of accuracy and availability of data points in each case. These experimental results agree with the predictions of a simple model, the Franck-Condon model,[3] if one assumes in addition that thermal vibrations of the lattice surrounding the absorption center can be represented by an effective harmonic oscillator of frequency ω_{eff}.[3] For the type of vibration that is generally thought to be effective, the Franck-Condon model predicts — already in its simplest semiclassical version — the shape and temperature variation of the halfwidth which

was found experimentally. So theory and experiment are in excellent agreement if one limits the experimental determination of the band shape to values larger than 1% of the absorption maximum.

In contrast measurements have been carried out far into the low energy tail of the first exciton band of pure alkali halides. In KI[4] an <u>exponential dependence</u> of the absorption constant on the photon energy (Urbach's rule) was observed over a range of <u>7 orders of magnitude</u> of the absorption constant: $K(h\nu) = K_o \exp\left\{-\sigma_o(h\nu_o - h\nu)/kT)\right\}$ with three constants K_o, σ_o, and $h\nu_o$. Similar results were obtained with KCl[5] and KBr[6] crystals and it was found that $\sigma_o = 0.80 \pm 0.02$ in all three cases.

A recent study of the optical characteristics of I^- ions[7] added in known concentrations to KCl single crystals closed the gap between these two different experimental results. For an appropriate concentration a low energy absorption band, due to the iodine ions, could be studied in great detail over a range of 4-1/2 orders of magnitude in absorption constant, including the region of maximum absorption as well as an appreciable part of the low energy tail. As reported previously[7] the experimental results can be described by a Gaussian curve from the band maximum to about 3% of the maximum absorption. For smaller absorption constants on the low energy tail the results can be fit well by Urbach's rule — that is, an exponential dependence of

the absorption constant on photon energy. This result gives us confidence in the assumption that Urbach's rule is a phenomenon intimately connected with electronic transitions in real vibrating lattices in ionic crystals.

This paper proposes a single formula covering both the range of absorption constants where a Gaussian shape has been found as well as the region of absorption constants where Urbach's rule has been verified. Especially for the absorption of the I^--ion in KCl a fit of the data points by the proposed new shape function could be achieved over the total measured range of 4-1/2 orders of magnitude of the absorption constant. In the following section the shape formula will be presented and compared with experimental results. The third section contains the theoretical background leading to the formulation of this general shape function.

EMPIRICAL SHAPE CURVE

Figure 1 reproduces the results of absorption measurements obtained from a solid solution of I^--ions in KCl single crystals.[7] The data points shown are taken from the results obtained with crystals of three different concentrations (10^{17}, 10^{18}, and 10^{19} I^--ions/cc approximately) at 300°K. Each single run consists of many measurements done with a great variety of sample thicknesses. All the data points were normalized and plotted vs. the normalized photon energy ($h\nu_{max} - h\nu$) in Fig. 1. Low photon energies are to the right. The dashed curve is an attempt to fit the results with a Gaussian curve. At low

absorption constants the agreement becomes increasingly poor.
The solid curve of Fig. 1 represents a proposed new shape
curve:

$$K(h\nu) = K_o \ e^{-\sigma(h\nu_o - h\nu)} \int\limits_{\alpha}^{+\infty} e^{-x^2} dx \qquad (1)$$

with $\alpha = -\left\{\tau(h\nu_o - h\nu) - \dfrac{\sigma}{2\tau}\right\}$ and σ and τ two constants.

As can be seen from Fig. 1, formula (1) fits the results
over the entire range of 4-1/2 orders of magnitude of the
absorption constant K. With K_o a known function of iodine
concentration and σ and τ known functions of temperature
(see reference 7), formula (1) describes all the results
obtained with the low energy absorption band of I⁻ in KCl
over its entire temperature and concentration range and an
enormous range of absorption constants.

The constants τ and σ were determined from a fit of
Urbach's rule (σ) and a Gaussian curve (τ) to the low energy
tail and the region around the maximum of the iodine
absorption band respectively. For the temperature range
covered by the measurements of reference 7 the temperature
variation of σ and τ was found to be given by:

$$\tau^2 = \frac{\tau_o^2}{kT} F(\omega_1) \qquad \text{and} \qquad \sigma = \frac{\sigma_o}{kT} F(\omega_2) \qquad (2)$$

where $F(\omega) = \dfrac{2kT}{\hbar\omega} \tanh\left(\dfrac{\hbar\omega}{2kT}\right)$. From a best fit of the measure-
ments by formula (1) the following parameters were obtained:

$$\sigma_o = 0.77; \quad \tau_o^2 = 0.87 \quad eV^{-1}; \quad h\omega_1 = 16 \times 10^{-3} \ eV;$$

$$h\omega_2 = 60 \times 10^{-3} \ eV.$$

Confidence in the applicability of formula (1), also to the exciton bands of pure alkali halides, is derived from the fact that Eq. (1) gives the correct asymptotic behavior for the low energy absorption tail. In this case $(h\nu_o - h\nu)$ is large and positive and thus α large and negative. The error function integral $\int_{-\alpha \ large}^{+\infty} e^{-x^2} dx$ is then a constant and consequently the absorption constant a purely exponential function of the photon energy (Urbach's rule). This property of Eq. (1) is asymptotic, that is, the smaller $h\nu$ gets the better it holds.

On the other hand for $h\nu$ larger than $h\nu_o$ ($h\nu_o$ is only approximately the position of the band maximum), α is large and positive. Thus, with increasing accuracy for increasing $+\alpha$, the integral of formula (1) can be approximated by

$$\int_{+\alpha \ large}^{+\infty} e^{-x^2} dx = \frac{e^{-\alpha^2}}{2\alpha} \left(1 - \frac{1}{2\alpha^2} \pm \ldots \right) \approx \frac{e^{-\alpha^2}}{2\alpha} \ .$$

With $-\alpha^2 = -\tau^2(h\nu_o - h\nu)^2 + \sigma(h\nu_o - h\nu) + const.$, we get approximately $K(h\nu) \sim e^{-\tau^2(h\nu_o - h\nu)^2}$, a Gaussian shaped function. Thus around the band maximum and on the high energy side

formula (1) predicts a bell-shaped curve in agreement with the experiments. Due to the narrowness of the error function the transition from an exponential behavior (Urbach's rule) to a Gaussian shape occurs in a narrow region of photon energies around $(h\nu_o - h\nu') = \dfrac{\sigma}{2\tau^2}$ at an absorption level $K(h\nu') = K_{max} \, e^{-\sigma/2}$. Thus for very large values of σ the exponential behavior of an absorption constant will only be seen at very low absorption levels. As σ increases with decreasing temperature, the exponential behavior will occur at relatively large absorption levels at low temperatures. (See comment on the KI exciton below.)

The whole family of curves for various temperatures has been calculated from formula (1) using the values of the constants obtained for the iodine absorption band in KCl. Figure 2 shows a plot of the normalized absorption constant K/K_{max} on a logarithmic scale vs. the normalized photon energy $(h\nu_{max} - h\nu)$ for the temperatures given. We want to emphasize that the position of the band maximum, $h\nu_{max}$, is different from $h\nu_o$ of formula (1). The calculation using the data of the iodine absorption band showed that the difference $h\nu_o - h\nu_{max} = 0.03$ eV at low temperatures and reaches the value 0.07 eV at 700°K. The temperature shift of the position of the band maximum which was found experimentally is therefore different from the corresponding shift of $h\nu_o$.

The halfwidths as determined from formula (1) are also different from the halfwidths due to a Gaussian curve of

9

parameter $\tau_0^2 = 0.87$ eV^{-1}. The Gaussian curve used to fit the data of Fig. 1 (dashed curve) would have a parameter $\tau_0^2 = 0.79$ eV^{-1}. This "Gaussian" halfwidth is related to parameters of Franck-Condon models. In the presence of an appreciable exponential tail one has to be careful, then, in the interpretation of the results obtained from measurements of the halfwidth and the maximum position of the absorption band.

The most extensive investigation of an exponential behavior of the absorption constant vs. photon energy was done at the long wavelength tail of the first exciton band of pure KI by Haupt.[4] Over 7 orders of magnitude of the absorption constant and in the temperature range from 20°K to 900°K Urbach's rule was established in a convincing way. All these measurements were done with single crystals or crystalline plates, molten between quartz plates. A comparison with results around the band maximum of the first exciton band of KI, obtained by Martienssen[6] with thin evaporated layers of KI, shows that the measurements of the evaporated films are not a continuation of the results obtained for the single crystals at low temperatures. This was interpreted as due to the fact that local disorder in the films broadens the absorption band above its "pure" width at low temperatures. This experimental difficulty makes it impossible to check rigorously formula (1) over its entire range in the case of exciton bands in pure alkali halides. This is because the special feature of formula (1) is its

<u>continuous</u> description of the absorption band from the tail to the band maximum. The applicability of the empirical formula (1) might, however, be derived from a statement given in the paper by Haupt:[4] "It is at smaller and smaller absorption constants that the measured curve deviates from the (exponential) behavior stated in formula...(Urbach's rule) at increasing temperatures. At 900°K this deviation starts at $K_1 = \frac{1}{20} K_{max}$, while at 500°K it starts only at $K_2 = \frac{1}{2} K_{max}$." As mentioned earlier the empirical formula (1) implies that the deviation from the exponential behavior starts at $K \sim e^{-\sigma/2}$. As $\sigma \sim \frac{1}{T}$ at high temperatures, $K_2/K_1 = e^{-T_1/T_2} = $

$e^{-\frac{500°K}{900°K}} \approx e^2 \approx 10$ as stated in reference 4. We are confident, then, that formula (1) describes also the entire range of the first exciton bands in pure alkali halides. Reliable experimental values of the absorption constant around the band maximum at low temperatures would however be needed for a rigorous check of the validity of formula (1) in these cases.

RELATION TO THEORETICAL MODELS

Various theoretical models[3,8] have been proposed to calculate the shape of absorption bands for an electronic dipole transition between ground and excited state at an absorption center in a real vibrating ionic lattice. In all models proposed for ionic crystals the energy difference ΔE between ground and excited state is assumed to be strongly

dependent on the instantaneous position of the ions surrounding the absorption center and is therefore critically affected by lattice vibrations.

Toyozawa[8] has recently analyzed the problem of Urbach's rule in connection with published experimental results of the shape of the first exciton band in pure alkali halides.[4-6] He assumed that the different mathematical description of the absorption curve around the band maximum and in the tail part of the first exciton band can be explained by an interaction of the electronic transition with two different types of lattice modes. Contributions to the absorption constant around the band maximum arise from those lattice modes Q_i which generate a <u>linear</u> dependence of the energy difference ΔE on the ionic displacements of this mode: $\Delta E = C_1 Q_i$. Toyozawa assumes that longitudinal acoustic modes are of this type. As a consequence the shape of the absorption constant around the band maximum is described by a Gaussian function:

$$K(h\nu) \sim \exp\left\{ -\tau^2 (h\nu_o - h\nu)^2 \right\}. \qquad (3)$$

On the other hand Toyozawa assumes that the absorption constant at the low energy tail of the exciton band is due to the interaction with other lattice modes Q_ℓ which give rise to an energy difference ΔE <u>quadratic</u> in the ionic displacements of this mode: $\Delta E = C_2 Q_\ell^2$. Toyozawa believes that longitudinal optical modes and transverse acoustical modes have this property. Using a Hamiltonian given by

Fröhlich, Toyozawa then calculates the shape curve due to
sole interaction with optical longitudinal modes. He gets
essentially an exponential behavior of the absorption con-
stant on the low energy tail (Urbach's rule):

$$K(h\nu) \sim \sqrt{\frac{1}{(h\nu_o - h\nu)}} \exp\left\{-\sigma(h\nu_o - h\nu)\right\} \quad \text{for } h\nu_o > h\nu \quad (4)$$

where

$$\sigma = \frac{\sigma_o}{kT} F(\omega_2) , \qquad \sigma_o = \frac{V_o}{18\pi(\frac{1}{K} - \frac{1}{K_o})(\frac{m}{\mu} K_o \alpha_H)^3} , \text{ and}$$

$$F(\omega_2) = \frac{2kT}{\hbar\omega_2} \tanh\left(\frac{\hbar\omega_2}{2kT}\right) .$$

V_o is the volume of the unit cell, $\hbar\omega_2$ the phonon energy
of the optical phonons (assumed to be all of the same
frequency), K and K_o are the static and optical dielectric
constants, μ the reduced mass of the formed exciton or
excitation and m the mass of the electron. Assuming $\mu = 0.65$ m
the measured values of σ_o in KI, KBr, and KCl can be
explained.

Toyozawa's approach will now be employed to calculate
the shape of the absorption band over its entire range. It
is assumed that both types of modes, Q_i ("linear") and
Q_ℓ ("quadratic"), interact with the electronic transition.
Furthermore formula (3) will be used to describe the
probability P_i that a photon of energy $h\nu_i$ will be absorbed
due to the interaction of a mode of type Q_i. Formula (4)

will be employed to describe the probability that a
photon of energy $h\nu_\ell$ will be absorbed under the action
of a lattice mode of type Q_ℓ.

The probability $P(h\nu_o - h\nu)$ that a photon of energy
$(h\nu_o - h\nu) = h\nu_i + h\nu_\ell$ is absorbed is then given by the
product $P_i(h\nu_i)P_\ell(h\nu_\ell)$. Both $h\nu_i$ and $h\nu_\ell$ may vary in
such a fashion that their sum: $h\nu_i + h\nu_\ell = h\nu_o - h\nu =$
constant. The probability $P(h\nu_o - h\nu)$ is therefore given
by an integral over the products $P_i P_\ell$ for all possible
values of $h\nu_i$ and $h\nu_\ell$ with $h\nu_i + h\nu_\ell =$ constant. This
gives:

$$P(h\nu_o - h\nu) \sim$$

$$\int\limits_{-\infty}^{+\infty} \int\limits_{o}^{+\infty} P_i(h\nu_i)P_\ell(h\nu_\ell) \; \delta\left[(h\nu_o - h\nu) - h\nu_i - h\nu_\ell\right] \; dh\nu_i dh\nu_\ell \sim$$

$$\int\limits_{-\infty}^{(h\nu_o - h\nu)} \exp\left\{-\tau^2(h\nu_i)^2\right\} \exp -\sigma\left\{(h\nu_o - h\nu) - h\nu_i\right\} dh\nu_i \sim$$

$$e^{-\sigma(h\nu_o - h\nu)} \int\limits_{\alpha}^{+\infty} e^{-x^2} dx \; ; \qquad \alpha = -\left\{\tau(h\nu_o - h\nu) - \frac{\sigma}{2\tau}\right\} .$$

14

The result is formula (1).

Two comments on formula (1) are in order:

(a) The derivation of formula (1) merely utilizes previously derived shape functions (formulas (3) and (4)). The physical understanding of the interaction of lattice modes with electronic transitions is therefore contained in theoretical models for the effect of the individual "linear" or "quadratic" interactions. The Franck-Condon model has been very successful to demonstrate graphically the particular influence of "linear" modes on the shape of absorption bands. A calculation of the absorption constant with a Franck-Condon model assuming "quadratic" interactions with Q_ℓ modes yields results which are not in agreement with the experiment. It remains to be seen if and how the result of Toyozawa's abstract calculations can be graphically demonstrated in Franck-Condon plots.

(b) Through the use of formula (4) the existence of lattice modes Q_ℓ with a quadratic contribution to the energy difference ΔE is postulated in all crystals where Urbach's rule has been verified experimentally. No rigorous theoretical proof of their existence has been given so far. Toyozawa[8] argued qualitatively that longitudinal, optical, and transverse acoustical modes are of the Q_ℓ type in their effects on excitons in pure alkali halides. For impurity absorption centers in alkali halides the existence of normal modes of Q_ℓ type is probable, but as yet unproven.

CONCLUSION

A new empirical shape formula for optical absorption bands is proposed which links a nearly Gaussian shape of the

absorption band near the band maximum with an exponential
behavior of the absorption constant on the low energy tail
of the band (Urbach's rule). In a special case the measured
absorption curve due to iodine ions diluted in KCl single
crystals is described by the new formula over 4-1/2 orders
of magnitude of absorption constant. Available data of the
shape of the first exciton bands of pure alkali halides
confirm conclusions drawn from the proposed formula.

ACKNOWLEDGMENT

16

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17

CAPTIONS

Fig. 1: The result of absorption measurements of a variety of
KCl crystals doped with 10^{17}, 10^{18}, and 10^{19} iodine
ions/cc is compared with the proposed new shape
function. The data, taken at 300°K, are plotted on
a logarithmic scale of the relative absorption con-
stant K/K_{max} vs. the normalized photon energy. The
solid line is a best fit of the experimental results
by Eq. (1). The dashed curve represents an attempt
to fit the data points by a Gaussian shaped function
(formula (3)). The lower abscissa refers to the
experimental results, the upper one shows the values
used for the calculation.

Fig. 2: The shape of an absorption band at various temperatures
calculated from the empirical shape function (1)
using the parameters obtained from experiments with
the iodine absorption band in KCl crystals. The
normalized absorption constant K/K_{max} is plotted on a
logarithmic scale vs. the normalized photon energy
$(h\nu_{max}-h\nu)$.

NORMALIZED ABSORPTION CONSTANT K/K_{max}

NORMALIZED PHOTONENERGY
$(h\nu_{max} - h\nu)$ IN 20